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Electrochemical response of a carbon paste electrode modified with the Methyl-2,4-bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1*H*,3*H*)quinazoline-8-carbodithioate ligand

Respuesta electroquímica de un electrodo de pasta de carbono modificado con el ligando 2,4-bis(ciclohexano)diespiro-1,2,3,4,4a,5,6,7-octahidro-(1*H*,3*H*)quinazolina-8-carboditioato de metilo

Navarro, Pedro[1*]; Contreras, Ricardo R.[2]; Nava, Oswaldo J.[1†]; Lacruz, Eveleydi[2]; Colt Vela, Greis[3]
[1]Laboratorio de Electroquímica. Departamento de Química.
Facultad de Ciencias, Universidad de Los Andes.
Mérida 5101, Venezuela
[2]Laboratorio de Organometálicos. Departamento de Química.
Facultad de Ciencias, Universidad de Los Andes.
Mérida 5101, Venezuela
[3]Laboratorio de Corrosión, Instituto de Tecnología Venezolana para el Petróleo (INTEVEP),
Los Teques, Miranda, Venezuela.
*pjnavarr@ula.ve

Abstract

The coordination chemistry of lead(II), an important environmental contaminant, was studied with the nitrogen-sulfur ligand Methyl-2,4–bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7–octahydro-(1H,3H)quinazoline-8-carbodithioate (L^{NS}). The spectroscopic evidence (UV/Vis, FTIR), mass spectrometry, thermal analyses (TGA and DSC), indicates the formation of [(L^{NS})(OH_2)(CH_3COO)Pb] with lead(II) as well as lead(IV). The L^{NS} ligand was used for the preparation of a carbon paste modified electrode and its electrochemical response was studied, showed an important enhancement for Pb(II) detection that permits lead determination at trace concentrations

Keyword: Chelating agent; lead; lead complexes, carbon paste modified electrode, cyclic voltammetry

Resumen

La química de coordinación del plomo(II), un importante elemento químico contaminante del medioambiente, se estudió utilizando el ligando nitrógeno-sulfurado 2,4-bis(ciclohexano)diespiro-1,2,3,4,4a,5,6,7-octahidro-(1H,3H)quinazolina-8-carboditioato de metilo (L^{NS}). La evidencia espectroscópica (UV/Vis, IRTF), espectrometría de masas, análisis termogravimétrico (TGA y DSC), indican la formación de un complejo tipo[(L^{NS})(OH_2)(CH_3COO)Pb] con plomo(II) y plomo(IV). El ligando (L^{NS}) fue usado en la preparación de un electrodo de pasta de carbono modificado, y su respuesta electroquímica fue estudiada con buenos resultados hacia de detección de plomo(II) en concentraciones traza.

Palabras clave: agente quelatante; plomo; complejos de plomo, electrodo de pasta de carbono modificado, voltametría cíclica

(†) In Memoriam

Introduction

Lead(II) ion is highly toxic and a remarkable synthetic efforts have been carried out to develop lead selective sensors especially in trace quantities. Chemically modified electrodes (CMEs) (Murray y col., 1987) have become important recently due to their versatility in clinical, environmental, and bio-technical analyses. One important approach to increase sensitivity and selectivity of CMEs in voltammetric procedures is analyte pre-concentration via chemical reactions (Kalcher 1990). Several review articles (Wang 1993, Abruma 1988, Janata y col., 1994) and books (Murray 1992) have introduced CMEs techniques. The pre-concentration agent (ligand, ion exchanger, etc.) is commonly introduced into the surface as part of an appropriate polymeric base or by mixing with a carbon paste matrix (Wierl y col., 1985). These CMEs, carbon paste electrodes (CPEs) have been used to determinate metal ions or organic analytes using appropriate chelating agents: dimetylglyoxime to determine nickel(II) (Baldwin y col. 1986), di-(2-iminocyclopentylidinemercaptonethyl) disulfide (Alemu 1998) and *N*-phenylcinnamohydroxamic acid (Gholivand y col., 2010) for copper(II), Glyoxal Bis(2-hydroxylanil) (Sook y col., 1995), for mercury(II) and silver(I), benzoin oxime (Goubert-Renaudin y col., 2009), dibenzo-18-crown-6 (Shamsipur y col., 2001), and 1,4-bis(prop-2'-enyloxy)-9,10-anthraquinone (Mousavi y col. 2001) for lead(II), *n*-octylpyridinium hexafluorophosphate (ionic liquid) for cadmium(II) and lead(II) (Ping y col., 2011), tyrosine for diclofenac sodium (Chethana y col., 2012), nevirapine for paracetamol in presence of folic acid (Tanuja y col., 2017). New methodologies have been developed recently based on using nanotechnology, for example: ferrimagnetic nanoparticles for detection of estriol (da Silveira y col., 2017), multi-walled carbon nanotube decorated with silver nano-particles in detection of Ferulic acid (Erady y col. 2017), ZnO-CuO nanoplates for dtermination of 6-thioguanine and folic acid (Beitollahi y col., 2016. Chelating agents with basic N, S, and O donating atoms with different Pearson hardness (Pearson 1997), modulate the metal ion and electrode surface interaction by preferential coordination: N and O for intermediate hardness acids such as nickel(II) and copper(II) and S for soft acids as lead (II) and mercury(II). In this article, the design and evaluation of a new CME system is described, suitable for selective pre-concentration and quantification of lead(II). The surface modifier chosen for lead(II) is methyl-2,4-bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1*H*,3*H*)quinazoline-8-carbodithioate ($\mathbf{L}^{\mathbf{NS}}$) ligand (Contreras y col., 2001). It is well known that thiosemicarbazides and thiosemicarbazones chelate soft metal ions type Pb(II) and Hg(II) (Michel, 1975, Davidovich y col., 2010), so it is possible to enhance the selectivity and sensitivity of lead(II) determination using a CME modified with this type of compound (Jianying y col., 1999, Perlado y col., 1995).

Material y Methods

Reagents and methods

All reagents were analytical-reagents grade. Nujol (Aldrich, 0.88 $g.mL^{-1}$), Graphite powder (Fischer Chemical GG7-500), $Pb(NO_3)_2$ (Strem Chemical), KCl (Merck) and $HClO_4$ (Analar), were used directly. Solvents and carbon disulphide were purified as described in the literature (Gordon, 1972). A standard lead (II) solution, 1×10^{-3} mol L^{-1} was prepared by dissolving $Pb(NO_3)_2$ in Millipore 18 MΩ.cm water.

Physical measurements

UV-vis spectra of compounds (chloroform solution) were recorded in a Shimadzu UV/Vis Uvmini-1240 spectrophotometer. FTIR spectra (5000 – 400 cm^{-1}, KBr pellets) were taken in a Fourier Transform Perkin-Elmer 1725X spectrophotometer. Room temperature ^{1}H and ^{13}C NMR spectra (DMSO), were taken in a Bruker Avance DRX 400-MHz spectrometer. Mass spectra were obtained with a Hewlett-Packard System 5988A GC-MS spectrometer using electronic impact ionization. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done in a TA SDT Q 600 Equipment. Electrochemical measurements were carried out in a EG & PAR 273A equipment, using a three electrodes cell, with a chemically modified carbon paste electrode as working electrode, a Ag/AgCl (3.5 mol L^{-1}) reference electrode and 0.1 mol L^{-1} KCl as supporting electrolyte. A platinum wire was used as an auxiliary electrode.

Experimental

Synthesis of methyl-2,4–bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7–octahydro-(1H,3H)quinazoline-8-carbodithioate ligand ($\boldsymbol{L}^{\boldsymbol{NS}}$)

The ligand ($\mathbf{L}^{\mathbf{NS}}$) was prepared according to the literature method (Contreras y col., 2001), and the structure corroborated by infrared, mass spectral and ^{1}H and ^{13}C NMR data comparison.

Synthesis of the lead-($\boldsymbol{L}^{\boldsymbol{NS}}$) complexes

A suspension of 1 mmol of lead (II) or lead(IV) hydrated acetate in 5 mL of hexane/methanol (8:2 v/v) was added drop-wise with stirring, to a solution of 0.3 g (1 mmol) of $\mathbf{L}^{\mathbf{NS}}$ ligand in 20 mL of hexane. After 1 hour reflux, the colored solid was washed with a minimum amount of diethyl ether and suction collected using a Millipore (0.8 μM) filter. The complexes formed decompose above 150 °C. ($\mathbf{L}^{\mathbf{NS}}$)Pb(II): green, yield: 0.3138 g (49 %); ($\mathbf{L}^{\mathbf{NS}}$)Pb(IV): olive green, yield: 0.1664 g (26 %). MS (CI) $P^{+\bullet}$, *m/z*: [($\mathbf{L}^{\mathbf{NS}}$)Pb(II)], $PbC_{20}H_{32}N_2S_2$ calc.: 571.81, found: 571.45;

[($\mathbf{L}^{NS}$)(OH_2)Pb(II)], $PbC_{20}H_{34}ON_2S_2$ calc.: 589.83, found: 589.60; [($\mathbf{L}^{NS}$)(CH_3CO_2)Pb(II)], $PbC_{22}H_{35}O_2N_2S_2$ calc.: 630.86, found: 630.60; [($\mathbf{L}^{NS}$)Pb(IV)], $PbC_{20}H_{32}N_2S_2$ calc.: 571.81, found: 571.25; [($\mathbf{L}^{NS}$)(OH_2)Pb(IV)], $PbC_{20}H_{34}ON_2S_2$ calc.: 589.83, found: 589.50; [($\mathbf{L}^{NS}$)(CH_3CO_2)Pb(VI)], $PbC_{22}H_{35}O_2N_2S_2$ calc.: 630.86, found: 630.60. FTIR vibrational spectra band positions and assignments, ν (cm^{-1}) (s = strong, m = medium, w = weak, br = broad); ($\mathbf{L}^{NS}$)Pb(II): ν(O-H), 3500m; ν(N-H), 3448m,br and 3288m; ν(C-H), 2932m; ν_a(C=C)+ν_a(C=N)+ν_a(C(=O)O), 1589s; ν_s(C=C), 1442s; ν_s(C=N)+ν_a(C=S), 1414s; ν_s(C(=O)O), 1348m; ν_a(S-CH_2-), 1248m; ρ-CH_2, 936m; ν_a(CSS-), 886w; ν_s(CSS-), 662w. ($\mathbf{L}^{NS}$)Pb(IV): 3508m; 3448w, 3288m; 2932m; 1589s; 1442s; 1422s; 1348m; 1248m; 936m; 886w; 662w. Electronic spectral data, λ (cm^{-1}) (ε , $M^{-1}cm^{-1}$); ($\mathbf{L}^{NS}$)Pb(II): 240(9,469); 317(8,688); 400(19,263); 537(210). ($\mathbf{L}^{NS}$)Pb(IV): 239(9,313), 316(12,286); 400(27,731).

Electrode fabrication

The CPE was prepared mixing 0.3 g of graphite powder with 5 to 15 % in weight of chemical modifier agent $\mathbf{L}^{NS}$ in an agate mortar; 175 μL of mineral oil (Nujol) was added and the mixture ground in an agate mortar. Unmodified carbon paste was prepared in the same way without $\mathbf{L}^{NS}$. The CPE modifier with [Pb(II)-$\mathbf{L}^{NS}$] and [Pb(IV)-$\mathbf{L}^{NS}$] was prepared adding 1.05 x 10^{-3} g of complexes to 0.3 g of graphite powder and 175 μL of mineral oil. The modified carbon paste was packed into a Teflon-tube electrode (0.6 mm i.d.) with a steel wire as electrical contact.

Electrochemical procedure

The fresh surface was activated through 15 cycles in the -800 to 0 mV range and 150 mVs^{-1} scan rate. Lead (II) preconcentration was done by first washing the electrode surface with Millipore 18 MΩ.cm water and then introducing in the corresponding lead (II) acetate solution with adjusted pH, and stirring for 5 min. The general parameters for cyclic voltammetry were: 40 mVs^{-1} and -800 to 0 mV scan range. The electrode surface was regenerated applying the same conditions of preconditioning. The general parameters for differential pulse voltammetry were: 8 mVs^{-1}, 75 mV pulse height, 0.5 s pulse width; and -800 to 0 mV scan range; the solution was deoxygenated by N_2 bubbling for 5 min.

Results and discussion

Lead-$\boldsymbol{L^{NS}}$ complexes characterization

The physicochemical properties of lead complexes are summarized in the Experimental Section. The compounds shows two types of νN-H stretchings: a weak, broad band at 3448 cm^{-1} due to the chelating secondary amine, where there is an important charge delocalization, and a fine medium intensity band at 3288 cm^{-1} assigned to the other secondary amine. At 1589 cm^{-1} there is an intense band assigned to a mixed ν_a(C=C)+ν_a(C=N)+ν_a(C(=O)O) stretching. The ν_a(CSS-) band is unsplit, indicating a possible bidentate sulphur chelation, as proposed by Contreras (Contreras y col., 2004). Broad bands at 3500 cm^{-1} indicate coordinated or/and lattice water molecules present. Metal complexes electronic absorptions spectra show three bands in the 400 – 240 nm range, assigned mainly to $\pi \rightarrow \pi^*$ internal ligand transitions. Mass spectra data for metal complexes show peaks attributable to [($\mathbf{L}^{NS}$)Pb]$^+$, [($\mathbf{L}^{NS}$(OH_2)Pb]$^+$, and [($\mathbf{L}^{NS}$)(CH_3COO)Pb]$^{+\bullet}$, in a mononuclear complex as suggested by the metal isotopic study ($^{208}Pb/^{206}Pb$), accompanied by a mass scan up to 2,000 m/z, to discard cluster impurities. The fragmentation pattern is consistent with sequential loss of peripheral molecular groups, previously observed in complexes with similar ligands (Contreras y col., 2010). The low peak abundance is most probably due to high metal complexes fragmentation under electronic impact ionization. Thermal analyses showed metal complexes decomposition without melting above 250 ºC. The DSC study shows an endothermic peak, centered in the 190 °C -200 ºC range, indicating loss of coordinated water molecules according to the TGA analysis. The spectroscopic, thermal and mass spectra data indicates a possible [($\mathbf{L}^{NS}$)(OH_2)(CH_3COO)Pb] structure for the lead(II) and lead(IV) complexes, shown in Fig. 1, which corresponds to a minimum energy computational structure (Wavefunction Inc., 2013).

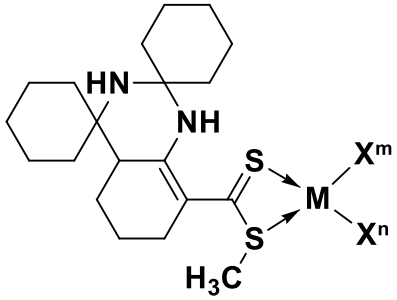


Fig. 1: Proposed structure of [methyl-2,4-bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1*H*,3*H*)quinazoline-8-carbodithioate]MX^mX^n, M = Pb(II) or Pb(IV) and X^m= CH_3COO^-; X^n = H_2O.

Effect of pre-concentration time and carbon paste composition

The anodic current dependence with pre-concentration time was studied for 1 x 10^{-6} and 1 x 10^{-7} mol L^{-1} Pb(II) concentrations, from 0 to 12 min. range. The current reaches an optimum value in 5 min., being constant thereafter; this suggests that the Pb(II) ion reaches equilibrium with the coordination sites of the chemical modifier. The effect of carbon paste composition on the pre-concentration was tested. The

CMEs prepared from 0, 3.5, 7, 11, and 15 % weight-to-weight ratio (w/w) $\mathbf{L}^{NS}$ - carbon paste were examined under the same conditions by differential pulse voltammetry in the -800 to 0 mV range, KCl 0.1 mol L^{-1} / $HClO_4$ 0.01 mol L^{-1} as supporting electrolyte and 5 min. accumulation time. It shows a gradual increase with a current maximum for a 7 % ratio, indicating that the modifier accumulated lead ions from the solution into the electrode surface. After this maximum, the current decreases with $\mathbf{L}^{NS}$ % increases suggesting that the modifier increases the resistance of the graphite phase.

Effect of the solution pH and supporting electrolyte

The pH effect (1 to 6 range) in the accumulation medium is shown in Fig. 2. At pH values below 3, the oxidation current diminishes, possibly by competition between the protons and the metal ions for the coordination active sites in the chemical modifier $\mathbf{L}^{NS}$. The current is relatively constant from pH 3 to 6.

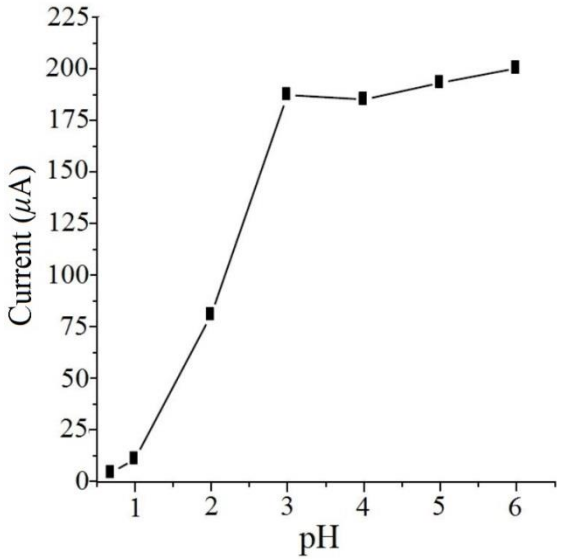


Fig. 2. pH effect (1 to 6 range) in the accumulation of Pb (II) 1 x 10^{-2} mol L^{-1}, using the carbon paste modified with $\mathbf{L}^{NS}$ electrode.

The $HClO_4$ concentration effect on the oxidation current is shown in Fig. 3. A maximum in the anodic current was observed at $HClO_4$ concentrations of 1 x 10^{-2} mol L^{-1} for the KCl/ $HClO_4$ electrolyte. The current values are smaller with $NaNO_3$/$HClO_4$ as supporting electrolyte. This indicates that the KCl/$HClO_4$ supporting electrolyte possibly stabilizes better the [($\mathbf{L}^{NS}$)Pb] complexes or intermediates formed on the electrode surface, since the Cl^- ion is a good ligand for lead and could complete the coordination sphere of the metal ion. In both cases there is a gradual decrease with increasing $HClO_4$ concentration, probably due to the pH effect. (Fig. 3).

The electrochemical behavior for Pb(II) 1 x 10^{-2} mol L^{-1} on carbon paste electrode without modifier, in KCl/$HClO_4$ is shown in Fig. 4. The cyclic voltammogram shows three processes: first, an anodic peak (A_1) at -440 mV; second, an anodic peak (A_2) at -356 mV and third, a reduction peak at -560 mV. A_4

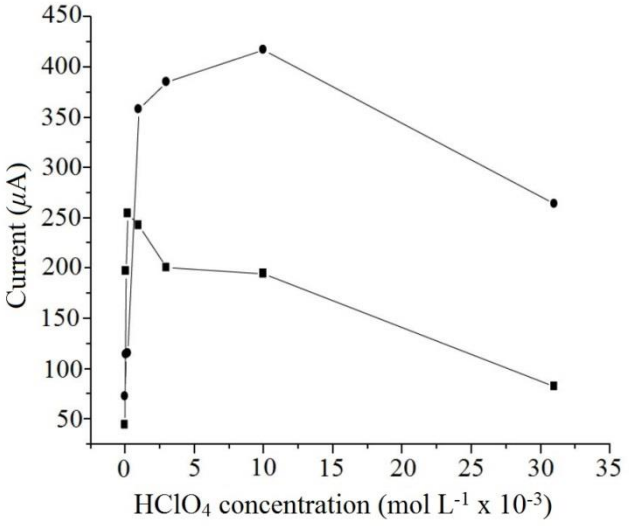


Fig. 3. Supporting electrolyte effect in the anodic current of Pb (II) 1 x 10^{-2} mol L^{-1}, (-▪-) KNO_3 0.1 mol L^{-1} / $HClO_4$, (-●-) KCl 0.1 mol L^{-1} / $HClO_4$.

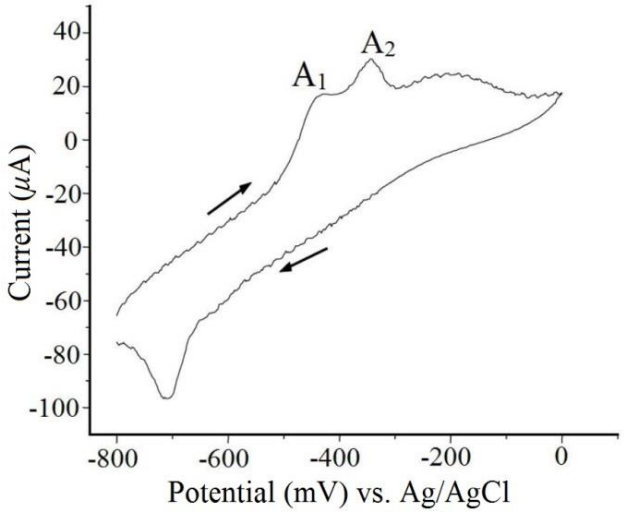


Fig. 4. Cyclic voltammograms of Pb (II) 1 x 10^{-2} mol L^{-1}; 40 mV s^{-1} scan rate, KCl 0.1 mol L^{-1} / $HClO_4$ 0.3 mol L^{-1} electrolyte. Carbon paste electrode without modifier.

Electrochemical behavior of lead(II) on the chemically modified carbon paste electrodes Cyclic voltammetry of the CME in KCl 0.1 mol L^{-1} as supporting electrolyte is shown in Fig. 5. The voltammogram corresponding to the modifier chemical agent $\mathbf{L^{NS}}$ (A) indicates no electroactivity in this potential range. The voltammogram for Pb (II) 1 x 10^{-2} mol L^{-1} (B) shows an anodic peak at -440 mV and a cathodic peak at -660 mV, both irreversible systems. Compared with the unmodified CPE shown in Fig. 4, there is a noticeable enhancement of Pb (II) response for the same ion concentration on the CME (Fig. 5).

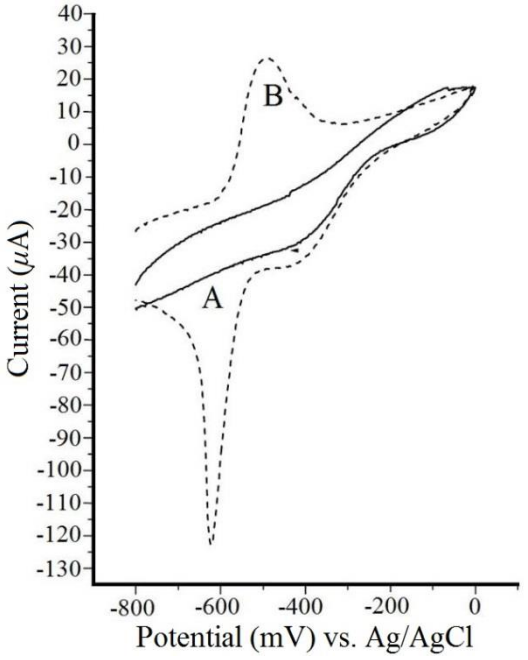


Fig. 5. Cyclic voltammograms: (A) Chemical modifier agent $\mathbf{L^{NS}}$, (B) Pb(II) 1 x 10^{-2} mol L^{-1} on carbon paste electrode modified with $\mathbf{L^{NS}}$. 40 mV s^{-1} scan rate, KCl 0.1 mol L^{-1} electrolyte.

In order to verify possible lead complex formation on the electrode surface, the CME was modified directly with the [($\mathbf{L^{NS}}$)Pb] complexes previously synthesized and characterized (2% w/w Pb(II)-$\mathbf{L^{NS}}$ or Pb(IV)-$\mathbf{L^{NS}}$ / graphite). The cyclic voltammetric measurements were made after 10 s of pre-reduction at -800 mV (Fig. 6). The cyclic voltammetric response for CME modified with Pb(II)-$\mathbf{L^{NS}}$, gives one anodic peak at -226 mV (A_1), attributed to Pb(0) oxidation to Pb(II) with the lead bonded to the carbodithioate site (sulfur-sulfur coordination); no reduction peak is observed in the inverse scan, probably due to the non conductor Nujol binder used, which inhibits or passivates the electrochemical reaction (Kalcher y col., 1995, Graner y col, 1993). The cyclic voltametric response for CME modified with [($\mathbf{L^{NS}}$)Pb(IV)], gives two anodic peaks (B_1 and B_2) at -232 and -378 mV respectively, attributed to different lead coordination forms. Initially in the pre-reduction cycle, all the Pb(IV) bonded to the carbodiothioate site is reduced to Pb(0); next in the B_1 oxidation process Pb(0) is oxidized to Pb(II). The B_2 oxidation peak was attributed to Pb(0) oxidation to Pb(II) of lead bonding to an imine site (nitrogen-sulfur coordination), possibly from a minimum quantity of the original [($\mathbf{L^{NS}}$)Pb(IV)] complex with this structure, possible for the harder Pb(IV) center.

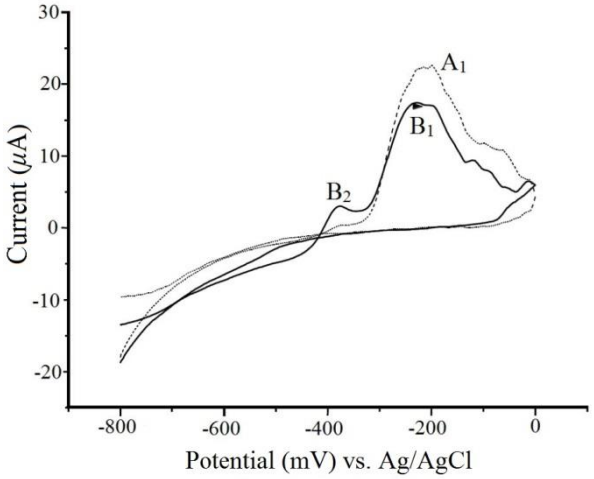


Fig. 6: Cyclic voltammograms on carbon paste electrode modified with lead complexes: A) [Pb(II)- $\mathbf{L^{NS}}$], (---); B) [Pb(IV)- $\mathbf{L^{NS}}$], (—); 40 mV s^{-1} scan rate; KCl 0.1 mol.L^{-1} / HClO4 0.01 mol L^{-1} electrolyte.

Comparing the oxidation potentials for free lead(II) accumulated in open-circuit from solution, with the potentials corresponding to the CPE modified with [($\mathbf{L^{NS}}$)Pb(II)] there is a correlation, which supports possible complex formation on the electrode surface. The mechanism of CME reactions could be attributed to the following steps:

1) Pre-concentration step:

$$Pb(II)_{free} + \mathbf{L^{NS}}_{surface} \rightarrow [Pb(II)\text{-}\mathbf{L^{NS}}]_{surface}$$

2) Pre-electrolysis step:

$$[Pb(II)\text{-}\mathbf{L^{NS}}]_{surface} + 2e^- \rightarrow [Pb(0)\text{-}\mathbf{L^{NS}}]surface$$

3) Measurement step:

$$[Pb(0)\text{-}\mathbf{L^{NS}}]_{surface} \rightarrow [Pb(II)\text{-}\mathbf{L^{NS}}]_{surface} + 2e^-$$

Calibration graph, detection limit, reproducibility and interferences

Differential pulse voltammograms at different Pb(II) concentrations under optimum conditions are shown in Fig. 7-A. Peak current increases linearly with increasing concentration up to 4.0 x 10^{-5} mol L^{-1} Pb(II). Fig. 7-B shows the calibration graph with a linear range from 1.93 x 10^{-5} mol L^{-1} (4 ppm) to 9.65 x 10^{-5} mol L^{-1} (20 ppm), the highest

concentration studied. The regression equation for the calibration graph is i_p = 0.7985 [Pb(II)] - 0.704, with a correlation coefficient of 0.992. The detection limit is 1.45 x 10^{-5} mol L^{-1} for 5 min. The relative standard deviation for 2 x 10^{-5} mol L^{-1} lead is 6 %.

The interference of other metallic ions was studied observing changes in the Pb(II) (1 x 10^{-5} mol L^{-1}) anodic peak current, upon addition of different ions from 1 x 10^{-3} mol L^{-1} to 1 x 10^{-4} mol L^{-1} concentration range. Na(I), K(I), Ca(II), Hg(II) metal ions, do not give any peak under the described conditions on the electrode with $\mathbf{L^{NS}}$ chemical modifier agent. Ni(II), Co(II), Cu(II), Zn(II) metal ions were studied because of their reactivity with the $\mathbf{L^{NS}}$ ligand; in fact, metal complexes with the $\mathbf{L^{NS}}$ ligand and these metal ions have been synthesized and characterized (Contreras, 2003). At high concentrations of these metal ions the Pb(II) signal diminishes, probably because of competition for the bonding sites of the modifier. Additionally, the molar excess of Cu(II) ion interferes significantly by decreasing the Pb(II) signal, probably due to formation of a Pb-Cu especies on the electrode surface (Hart y col., 2001, Gunasinghan y col., 1991).

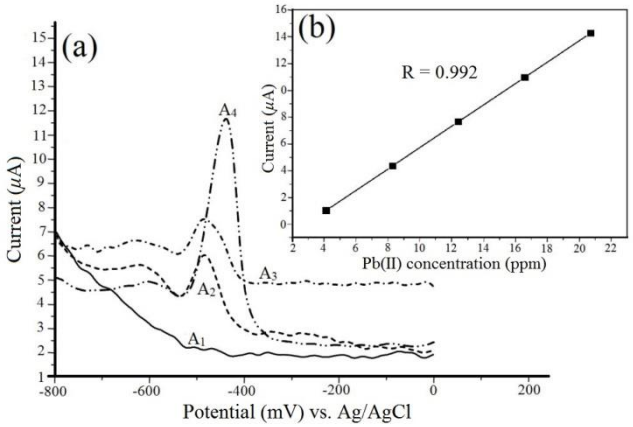


Fig. 6: (A) Differential pulse voltammogram of: A_1) 0.0 mol L^{-1}; A_2) 4.0 x 10^{-5} mol L^{-1}; A_3) 6.0 x 10^{-5} mol L^{-1}; A_4) 8.0 x 10^{-5} mol L^{-1} Pb(II) solutions. 8 mV s^{-1} scan rate, 75 mV pulse height; 0.5 s pulse width, 5 min. pre-concentration time, KCl 0.1 mol L^{-1} / $HClO_4$ 0.01 mol L^{-1} electrolyte. (B) Current vs Pb(II) concentration calibration plot.

Analytical application

The determination of lead(II) was then carried out in tap water, however, as expected, this method is not sensitive enough to determine the concentration of lead(II) at this level, which has been quoted to be extremely low: 0.042 ± 0.001 ppm, determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Hence, the determination was carried out in "spiked" tap water with a VARIAN lead standard solution. The analysis results are shown in Table 1.

Tabla 1. Table 1. Results of determination in tap water containing lead (added)[a]. The determinations were carried out with a ICP-AES Varian Liberty AX serie II, of the Laboratorio de Servicios Analíticos (LARSA). LD = 0.0016 ppm of lead.

Sample	Number of determinations	Lead added	Lead found	RSD (%)	Recovery of spiked (%)[b]
Tap water	8	2 x 10^{-5} mol L^{-1} (4.1 ppm)	2.2 x 10^{-5} mol L^{-1} (4.6 ppm)	7	110

[a] The sample was lightly acidified and heated by 5 min. The pH was adjusted to 7.
[b] The recovery is usually of 90 to 120 % (Simancas y col., 2006).

Conclusions

The spectroscopic evidence (UV/Vis., FTIR), mass spectrometry, thermal analyses (TGA and DSC), indicates the possible formation of [($\mathbf{L^{NS}}$)(OH_2)(CH_3COO)Pb] with lead(II) as well as lead(IV) with the new methyl-2,4-bis(cyclohexane)dispiro-1,2,3,4,4a,5,6,7-octahydro-(1*H*,3*H*) quinazoline-8-carbodithioate ($\mathbf{L^{NS}}$) ligand. Additionally, the new chemically modified carbon paste electrode, using $\mathbf{L^{NS}}$ as modifier, shows an important enhancement for Pb(II) detection that permits lead determination at trace concentrations. The above results show a very promising application in a simple and selective method with a low detection limit.

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Navarro, Pedro*: Doctor en Química por la Université Claude Bernard Lyon 1 (Francia). Ha sido Coordinador del Postgrado en Electroquímica Fundamental y Aplicada, Coordinador del Laboratorio de Electroquímica y del Área Docente de Química Analítica, Departamento de Química - ULA.*

Contreras, Ricardo.*: Doctor en Química por la Universidad de Los Andes. Coordinador General del Postgrado en Química Aplicada. Coordinador del Laboratorio de Organometálicos y del Área Docente de Química Inorgánica, Departamento de Química - ULA. Es Miembro Correspondiente Estadal de la Academia de Mérida. Correo electrónico: ricardo@ula.ve.*

Nava, Oswaldo: *Licenciado en Química egresado del Departamento de Química, Facultad de Ciencias de la Universidad de Los Andes. Hasta el momento de su fallecimiento en 2017, fue estudiante del programa de Maestría del Postgrado en Electroquímica Fundamental y Aplicada.*

Lacruz Eveleidy: *Doctora en Química Aplicada (Mención Estudio de Materiales) por Universidad de los Andes. Profesora Contratada en las áreas de Fisicoquímica y Química Inorgánica del Departamento de Química, Facultad de Ciencias de la Universidad de Los Andes. Correo electrónico: eklv@ula.ve.*

Colt Vela, Greis*: Magister en Electroquímica Fundamental y Aplicada por la Universidad de los Andes. Investigadora del Laboratorio de Corrosión, Instituto de Tecnología Venezolana para el Petróleo (INTEVEP), especailista téncio en el área de corrisión y evaluación de tratamientos químicos. Correo electrónico: coltg@pdvsa.com.*